

Direct Transformation of Vacancy Voids to Stacking Fault Tetrahedral

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It is well established that materials, upon irradiation, exhibit embrittlement and swelling that can often be traced to the atomic scale processes of defect accumulation. Defects (interstitials and vacancies) are produced; these diffuse and aggregate, leading to interstitial and vacancy clusters. When a supersaturation of vacancies is created, vacancy clusters can grow to the point that the material swells and fails. Here we report on our recent, unexpected observation that a vacancy void can thermally transform directly to a stacking fault tetrahedron (SFT) without passing through a Frank loop, the pathway previously postulated for the formation of SFTs in metals [1].

The simulations described here were done using parallel-replica dynamics (PRD) [2], an accelerated molecular dynamics method developed at LANL, in which time is parallelized. With PRD, given M processors, a speedup over molecular dynamics (MD) of up to a factor of M is possible. We used $M=39$ and obtained speedups between 23 and 31. Nudged elastic band (NEB) calculations were then used to build state-to-state minimum energy paths. The Cu-Cu interaction was described using the embedded atom method (EAM) [3,4].

We performed PRD at constant volume on a 20-vacancy void at 400 K. After a phase lasting 1.35 μs in which the extra vacancy diffused on the surface of the void, the extra vacancy reached an octahedral vertex, as illustrated in the inset of Fig. 1. Shortly thereafter, the void underwent a surprising transformation: as the vacancy executed a hop around the vertex, the corresponding moving Cu atom entered the void, triggering relatively direct collapse of the void into an SFT. Also surprising is that a process with such a high barrier (2.25–2.70 eV; see Fig. 1) could occur on this time scale. Assuming the rate is Arrhenius [$k=\nu \exp(-\Delta E/k_B T)$, where k_B is the Boltzmann constant] and a standard prefactor $\nu=10^{13}/\text{s}$, it would take $\sim 10^6$ years for this event to occur. In contrast, we observe first-passage times $\tau=1/k$ between 1 and 15 ns (once the void reaches the octahedral vertex state). Estimating the prefactor from the bold path in Fig. 1, with $\tau=5.9$ ns and $\Delta E=2.25$ eV, we find $\nu=4\times 10^{36}/\text{s}$, a factor of 10^{25} higher than the standard value. We also

find a Vineyard prefactor (computed from the normal modes of the system at the minimum and saddle [5]) of $\nu=5\times 10^{42}/\text{s}$. These prefactors are more than 20 orders of magnitude larger than any prefactor we are aware of for processes in metallic systems, indicating that something unusual is happening.

This extremely high prefactor means that the transition state has a much higher entropy than the initial state, which we believe in this case results from an unusual volume effect. As the void collapses, the effective volume of the system increases as the material gains access to the empty space in the void—volume that was formerly excluded from it. For an isothermal system, when the system volume changes by ΔV , the entropy changes by approximately [6] $\Delta S=\alpha B \Delta V$, where α is the coefficient of volumetric thermal expansion and B is the bulk modulus. Using values for α and B as predicted by this EAM potential, and assuming the transformation of a 20-vacancy void increases the effective system volume by 10 atomic volumes at the transition state, the entropy change is $\Delta S=67.5 k_B$. This predicts a rate prefactor increase of $\exp(67.5)\sim 10^{29}$, consistent with the observation above.

This void-to-SFT collapse can also occur for larger voids. For example, Fig. 2 shows the transformation of a 45-vacancy void, which collapsed after 0.25 μs at $T=475$ K. As in the case of the smaller void, the potential energy barrier is very large, over 4 eV, and the transformation is again driven by a large entropy increase.

Although it is not yet clear whether this void-collapse mechanism is important under typical radiation damage conditions, its existence illustrates that even the simplest of materials can behave in complex and unexpected ways that we are just beginning to understand. Accelerated molecular dynamics methods [7] offer a powerful tool for investigating these behaviors, as the dynamics often take place on time scales that are inaccessible to direct molecular dynamics.

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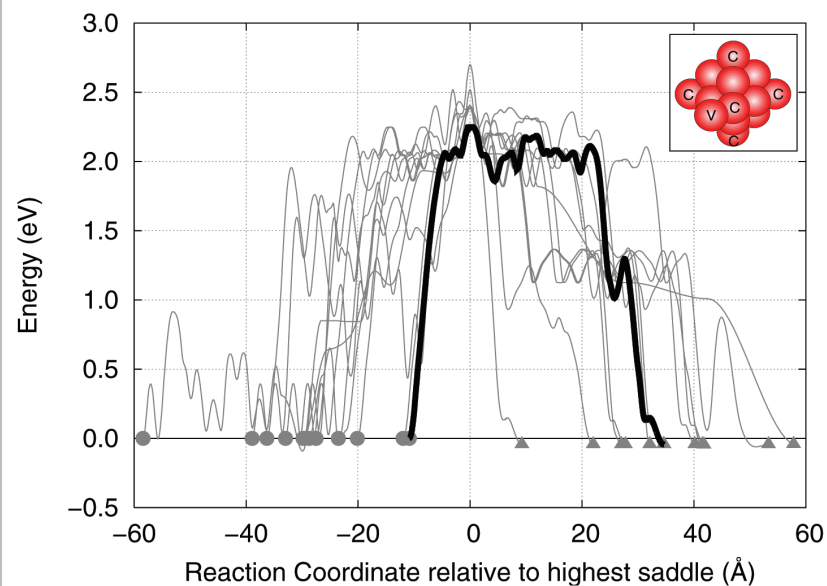


Fig 1. Inset: The 20-vacancy void in Cu. In this display convention, red spheres are vacancies. Notice the extra vacancy (labeled V) near one of the vertex sites (labeled C). Main Figure: Minimum energy path for the transformation of a 20-vacancy void to a SFT from 12 MD simulations started at the vertex state. The reaction coordinate has been shifted so that the highest energy saddle of each path is at 0. The circles and triangles represent the beginning and the end of each path.

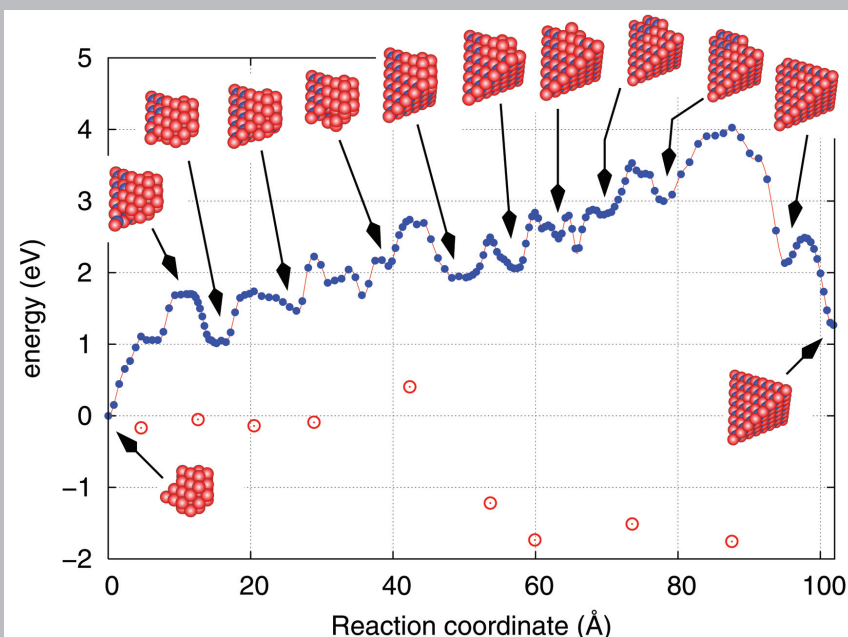


Fig 2. Minimum energy path for the transformation of a 45-vacancy void to a SFT. The inset figures are minima from the parallel-replica simulation (red spheres are vacancies, and blue spheres interstitials, relative to an initial FCC reference structure). The open circles are estimates of the free energy along the path.